PATENT
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Allison H. SAMPSON, et al. | Group Art Unit: 1754

Serial No. 10/053,666 | Examiner: Ngoc-Yen Nguyen

Filed: August 2, 2001

For: METHODS FOR MAKING CHLOROUS ACID AND CHLORINE DIOXIDE

DECLARATION OF ALLISON H. SAMPSON

Commissioner of Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Allison H. Sampson, do hereby declare the following:

1. I reside in 8622 Raintree Woods Dr, Fair Oaks Ranch, TX 78015, and am currently employed by Dripping Wet Water, Inc. which is also located at the same address.

2. My educational background is set forth on my Curriculum Vitae ("CV") attached hereto as Attachment A. As indicated, I have a Bachelor's degree in Chemical Engineering from Texas Tech University of Lubbock, TX.

3. My professional experience, which is also set forth on the attached CV, Attachment A, includes over 19 years of experience in various technical, marketing, and management roles in the Water Purification and Treatment field. As a result of my education and experience, my professional contemporaries and colleagues consider me an expert in the water purification and treatment field.

4. Based upon my education and experience, I have an opinion regarding what the level of ordinary skill in the water purification and treatment field generally would be. Persons of ordinary skill in this art would include not only those individuals skilled in chemical engineering, but also those working with water purification and treatment. More particularly, persons of ordinary skill in this art would especially include those in the water treatment fields of ion exchange and disinfection. In most cases, such persons would have at least a bachelor's degree in chemistry or chemical engineering, and would have at least several years of experience in ion exchange and water disinfection.

5. Drawing upon my expertise in this industry, I understand the level of ordinary skill in the art at the time the above-captioned application was filed (August 2, 2001) and can offer my expert opinion as to how persons of ordinary skill in the art would

perceive and respond to relevant art in the field of generation of chlorous acid and chlorine dioxide.

6. I have read and understood the Office Action of August 11, 2005.

7. The Examiner rejected claim 47 under 35 U.S.C. §112, first paragraph, stating that she could not find support for the claim limitation "...has a pH in the range of about 1.9 to about 2.9" in the specification. As you will note, the specification at page 26, line 15 to page 27, line 5, describes the generation of chlorous acid and chlorine dioxide in the presence of a cation exchange material in the hydrogen form and a catalyst (platinum). The example states that the resultant pH of the solution was pH 2.4 after having passed sequentially through the cation exchange resin to make $HClO_2$ and then through the catalyst to make the dissolved gas, ClO_2. Further support can be found in example 7A on page 28, line 13 to page 29, line 4. In example 7A, the same conditions result in a pH of 2.4 as well. This is clearly within the range claimed within claim 47, which refers to the generation of chlorous acid. In Attachment B, a graph was supplied by our cation exchange manufacturer, Resintech, Inc. (160 Cooper Road West Berlin, NJ 08091), for the CG-8 resin used in the examples in the specification. The starting concentration of the sodium chlorite

solutions in Examples 1 - 6 are described on page 16, line 2 - 4 as having a chlorite concentration of 823 ppm, which is approximately equivalent to 1101 mg/L $NaClO_2$. As one can see from the graph, if we look at where a concentration of 1101 mg/L $NaClO_2$ corresponds on the Y-axis, and move in the X-axis direction until we intersect the line. The pH value corresponding to 823 ppm ClO_2^- would be about 1.9. It is also noted that by equation (2) in the specification of the present invention, when $HClO_2$ is catalyzed to ClO_2, 4 moles of the H^+ ion are converted to 2 moles of water, thus increasing the pH of the resultant solution somewhat. Therefore, one of skill in the art would understand this to mean that the resulting chlorous acid solution would have a pH within the claimed range.

8. The Examiner rejected claim 49 under 35 U.S.C. §112, first paragraph, stating that she could not find support for the claim limitation regarding cation exchange materials. The Examiner stated that the description of cation exchange resins and materials described at page 13, lines 3-12 was directed toward their use for removing unwanted ions from the final solution and not for conversion of sodium chlorite to chlorous acid or chlorine dioxide. As I explained to the Examiner at our interview of September 13, 2005, one of skill in the art would not have read the recited paragraph (page 13, lines 3 - 12) describing the choice of cation and anion exchange materials as being limited to a particular use,

only because of the location of the paragraph within the text of the specification. While the paragraph prior to the one recited by the Examiner in the rejection does refer to methods of removing unwanted ions (page 12, line - page 13, line 3), the paragraph after the referenced paragraph (page 13, lines 13-23) teaches the cation exchange conversion of chlorite to chlorous acid. Moreover, the last sentence of the paragraph recited by the Examiner explicitly states, "Selection of a particular ion exchange material is considered within the skill of those knowledgeable in the field". As such, it is my opinion that one of ordinary skill would have understood that the examples in the recited paragraph were a sample of the cation and anion exchange resins commercially available for any of the processes disclosed within the specification, and not limited to removal of unwanted ions.

9. The Examiner rejected claim 49 under 35 U.S.C. §112, second paragraph, stating that the term "essentially pure" was not defined in the claim and the specification does not provide a standard for ascertaining the requisite degree of purity. In my experience, one of ordinary skill in the water purification art would understand that when a dilute sodium chlorite solution (such as 1101 mg/L) is passed through a strong cation exchange column in the hydrogen form, where the column is not exhausted, that conversion of the sodium chlorite to chlorous acid is going to be almost 100%. As such, the

chlorous acid effluent from the cation exchange column will be essentially a pure chlorous acid solution. Support for this is found in a graph from Resintech entered as Attachment C. In Attachment C, the graph shows how much $NaClO_2$ remains in solution after having passed through CG-8 resin regenerated under normal circumstances. A specific example shows that if CG-8 resin is well regenerated (>90% H), the effluent solution will have less than 0.8 mg/l $NaClO_2$ in it when the influent solution is 1000 mg/l $NaClO_2$. This means that the resultant effluent solution is >99% pure. Therefore, it is my opinion that one of ordinary skill in the water purification field would understand what the term "essentially pure" means when used in the context of claim 49.

10. The Examiner rejected claims 2-3 under 35 U.S.C. §102(b) as being anticipated by Callerame (USP 3,684,437) (Callerame '437). Callerame '437 states that it discloses a process for producing chlorous acid via passing an alkali metal chlorite solution through an ion exchange column, using a mixture of a cation exchange resin and anion exchange resin. It is my opinion that there are a number of scientific inconsistencies with what is purportedly taught in Callerame '437 and, as such, Callerame '437 does not teach the process of the present invention. I will discuss each of these inconsistencies and offer my opinion on why this reference does not anticipate claims 2-3 of the present invention.

11. In column 1, lines 44-47 of Callerame '437, the inventor states "Since chlorine dioxide absorbed in water forms chlorous acid from which the gas can be readily expelled by heating, chlorine dioxide and chlorous acid are for all practical purposes, the same thing." This statement is scientifically incorrect. See Attachment D which teaches the distinction between acidified sodium chlorite and chlorine dioxide. When the pH of the $NaClO_2$ is lowered into the range of neutrality as taught in Attachment D and the'437 patent (pH 6.2 - 7.0 by Callerame), Attachment D teaches that no ClO_2 is formed by the decomposition of the acidified $NaClO_2$ when exposed to heat. Applicants clearly distinguish between unstable chlorous acid and chlorine dioxide in their instant invention as not equivalent. Chlorous acid is an ionic species made up of hydrogen cation (H^+) and chlorite anion (ClO_2^-) which forms the ionic species $HClO_2$. Chlorine dioxide, on the other hand, is a non-ionic dissolved gas in solution, as is shown by its chemical formula in the Species Table in Attachment E.

12. Callerame '437 further states that in order to form chlorous acid (chlorine dioxide by Callerame '437 definition), sodium chlorite ($NaClO_2$) must be passed through both cation and anion resins in a mixed form. In contrast, Applicants' process cannot work if both cation and anion resins are used together in

their process. This is because the anion ClO_2^- would be bound to the anion exchange column, and the resulting effluent would be water.

13. In addition, Callerame '437 discloses that optimal results occur if the pH of the solution is between 6.2 and 7.0, preferably between pH 6.5 and 7.0. In contrast, it is impossible using Applicants' process, to make either chlorous acid or chlorine dioxide at this high pH. In fact, the Examples for making chlorous acid in the present application result in a pH of 1.9, and the pH of the chlorine dioxide solutions average about 2.4, before any additional pH adjustment. See paragraph 7 above for a discussion of pH.

14. The Examiner has suggested that Example 9 of Callerame '437, which is a purported control experiment, teaches conversion of sodium chlorite into chlorous acid using a strong cation exchange resin *without* the presence of an anion exchange resin, admitting however that the resulting exchanged solution contains only 0.3% ClO_2^-, which is approximately 27% conversion, compared to the 90% figures disclosed in earlier examples of Callerame '437. In my opinion, Example 9 does not teach the claimed process of the present invention for the following reasons. First, in addition to ClO_2^- ion, Callerame '437 shows the presence of OCl^- ions (0.3%) and HCl (0.3%). In contrast, the claimed process of the present application

requires the *direct* exchange of Na^+ ions with H^+ ions using only a cation exchange resin. This is shown by equation in Attachment E, as provided by ResinTech. At no time is there any reaction with the ClO_2^- ion. As shown in Attachment F, in the present invention there is no conversion of ClO_2^- ion into any other species, and 100% of ClO_2^- ion going into the column leaves as ClO_2^- ion. Second, it is chemically impossible, in my experience, for the ClO_2- ion in the process of the present invention, to be converted at any concentration to OCl^- or HCl. Third, the inventor in Callerame '437 reports the same pH of the product solutions even when he increases the concentration of sodium chlorite to 2%, which does not correlate with the cation exchange characteristics of the cation resin, as demonstrated in Attachment B. Therefore, I can only conclude as an expert in this field, that the actual process used in Callerame '437 is not our process, and therefore it cannot anticipate claims 2-3 of the present invention.

15. The inventor of Callerame '437 claims to have measured the amount of chlorous acid in the effluent solution by spectrophotmetry. As an expert in the field, I can state that there is no accepted spectrophotometric method for measuring chlorous acid in aqueous solution. It has been reported in Attachment G that chlorite can be measured spectrophotometrically at 260 mμ, but this reference is made in 1979, and no known accepted method commonly

exists today. It is also reported in Attachment G, that ClO_2 can be measured spectrophotometrically at 360 mμ. The inventor of Callerame '437 states that all readings were taken at 340 mμ. The only product that could possibly be measured spectrophotometrically at a wavelength of 340 mμ is chlorine dioxide, which has a distinct yellow color. In the examples of our process, we use the Hach Method 8138 (Attachment H), which has no interference with chlorous acid. The EPA standard method for analysis of chlorine dioxide can be found in EPA 815-R-05-008, Revision 1.1, dated May 2005 (Attachment I). The method uses titration instead of spectrophotometry to differentiate between the two species, ClO_2^- and ClO_2. In the first step, the ClO_2 gas is sparged from the solution with an inert gas so as to isolate the ionic ClO_2^-.

16. With regard to the term "additive" as used by the Examiner in the rejection of claim 3, cation exchange material can be used as the additive in many forms known to those skilled in the art. One can mix, layer, or otherwise add the additive to the primary cation exchange material. However, the'437 patent does not teach the claimed process of the present invention, as previously demonstrated. Therefore, the'437 patent does not teach cation resin as an additive.

17. The Examiner rejected claims 4-5 under 35 U.S.C. §102(b) as being anticipated by Callerame (USP 3,828,097) ("Callerame '097"). Callerame '097 states that it discloses a process for producing chlorous acid by flowing an aqueous solution of a metal chlorate and a nitrite through a cation exchange resin in the hydrogen form. I have carefully reviewed Callerame '097 and conclude that, as in Callerame '437, the process taught by Callerame '097 cannot be the same process as claimed in the present application for the following reasons. First, as in paragraph 11 above, the inventor claims that chlorous acid and chlorine dioxide are the same thing, which one of skill in the art would understand to be scientifically incorrect. Second, the claimed process of the present invention does not use nitrite or any other reducing agent to mix with the sodium chlorate prior to elution through the cation exchange column. Third, the term additive would be understood by one of skill in the art to be an insoluble substance added to the cation exchange resin while in the dry or moist form prior to use in the claimed process. As shown in Example 1 of Callerame '097, the sodium nitrite is added to the metal chlorate solution prior to passing it through the cation exchange column. As such, one of skill would not understand sodium nitrite to be an additive. Fourth, the inventor of Callerame '097 shows in Example 1, that the pH of the initial solution is 9 and then acid must be added for the conversion to occur. No acid is added to the metal chlorate

solution prior to its elution onto the column in the present invention. The only source of H+ ions is from the cation exchange column. In summary, one of ordinary skill in the art would readily understand that the process taught in Callerame '097 is not at all the same as the process claimed in claims 4-5 of the present application, and therefore Callerame '097 cannot anticipate the claimed process of the present invention.

18. The Examiner cited the Kross reference (USP 5,100,652) ("the '652 patent") as showing that acids and sugars with vicinal hydroxyl groups could be used as a catalyst as claimed, inter alia, in claims 42, and 43 to convert chlorous acid to chlorine dioxide. In my expert opinion, one of ordinary skill in the art would understand, from a careful reading of the specification of the present invention, that the catalysts used to convert chlorous acid to chlorine dioxide in the present invention are insoluble substances which can either be mixed with the ion exchange material prior to use or deposited on various substrates prior to use. At no time does the catalytic material used in the reaction become part of the effluent chlorous acid product. In the '652 patent, the sorbitol, or malic acid is added to the product prior to its use and is part of the end product. It is clearly stated at page 12, lines 1-9, of our application that many catalysts that can be used within the scope of the present invention. These include, but are not

limited to platinum, palladium, manganese dioxide, carbon, and ion exchange material. Further, it is well known that depositing such catalysts on various substrates, such as zeolites, aids in the catalysis by increasing surface area. Such catalysts are commercially available, and it is within the scope of those skilled in the art to choose an appropriate catalytic material and/or substrate to catalyze chlorous acid to chlorine dioxide. As such, one of skill in the art would not consider compounds having the vicinal hydroxyl groups as described in the '652 patent to be with the scope of the catalysts encompassed within the present invention.

19. It is my opinion that the subject matter claimed in the present invention would not have been obvious to one of ordinary skill in the art based upon the prior art cited and considered by the Patent Examiner, or any other prior art known to me, because until the present invention there had never been any teaching or suggestion in the art that one could make chlorous acid by contacting a metal chlorite solution with a cation exchange resin in the hydrogen form, or that chlorine dioxide could be made by generating chlorous acid in this manner and then catalytically converting the chlorous acid to chlorine dioxide as described in the present application.

20. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under section 1001 of Title 18 of the United States Code; and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

10/11/05

Date

Allison H. Sampson

Attachment A: CV of Allison H. Sampson

Attachment B: Resintech Graph, "Effluent pH vs. Feed Concentration of $NaClO_2$ Parameters are %H form of CG8"

Attachment C: Resintech Graph, "$NaClO_2$ Leakage vs Feed Concentration of $NaClO_2$ Parameters are %H form of CG8"

Attachment D: Excerpt of Gordon, Gilbert et al., The Chemistry of Chlorine Dioxide," S. J. Lippard (Ed.), in <u>Progress in Inorganic Chemistry</u>, Vol. XV, J. Wiley & Sons, New York, 1972, pp. 202-286